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Stereochemical Characterization and Antimicrobial Activities of Synthesized Ni (11), Cu (11) and Zn (11) Schiff Base Complexes Derived from P-Nitroaniline and Salicylaldehyde

Grace E. Iniama

Associate Professor, Department of Pure and Applied Chemistry,
University of Calabar, Nigeria

Isaac T. Iorkpiligh

Lecturer, Department of Education Oju- Benue State, Nigeria

Abasiama I. Alfred

Research Assistant, Department of Pure and Applied Chemistry, University of Calabar, Nigeria

Abstract:

A Schiff base ligand, *p*-nitroanilinesalicylidene and the corresponding Ni(11), Cu(11) and Zn(11) complexes were obtained from condensation reaction of *p*-nitroanilinesalicylidene with these metal(11) salts. These synthesized compounds were characterized by the use of elemental analysis, conductometry, magnetic susceptibility, IR, ¹H-NMR and UV-Vis spectroscopy. They were also screened for antimicrobial activities. From the spectral data, the ligand, a monobasic, bidentate molecule became deprotonated and coordinate to the metal ions through the phenolic oxygen and the azomethine nitrogen in a 2: 1 ligand: metal ratio giving square planar to Ni(11) and Cu(11) then tetrahedral geometrical configurations to the Zn(11) complexes. The ligand and the metal complexes exhibited some degree of antimicrobial activities against *Staphylococcus aureus*, *Echerichia coli*, *Candida albican* and *Aspergillus Niger*.

Keywords: Schiff base, synthesized, bidentate, square planar, antimicrobial activity

1. Introduction

Metal complexes derived from Schiff bases have for many decades now attained a height of great importance in various spheres of human endeavours. They are used in pharmaceuticals, chemical industries, agricultural sectors, corrosion and analytical studies [1-3]. The synthesis of metal complexes aroused great interest because of their versatile coordination behaviour and in the understanding of molecular configurations and processes [4]. The study of metal complexes of Schiff base ligands are particularly significant due to their structures, stability and their coordination chemistry. Schiff base complexes are considered to be among the most important stereochemical models in transition metal coordination chemistry as a result of their preparative accessibility and structural varieties [5]. They are variedly synthesized, characterized and most often their applications stemmed from their structural modifications. Schiff bases are versatile, those from aliphatic aldehydes are relatively unstable and can be readily polymerizable while those from aromatic aldehydes having effective conjugation systems, are more stable [6]. Metal complexes of these ligands are easy to prepare with structure- activity design relationship and often with resultant enhanced effectiveness [7][8]. The coordination abilities of Schiff base chelating ligands contribute immensely to their wide applications and significantly because of their easy reproducible nature. In many biochemical reactions, they appear as important intermediates in a number of enzymatic reactions involving the enzymes and amino or carbonyl group of the substrates [8]. Mechanistically, the first step in the formation of Schiff base involves the generation of a carboanion. which react with the lone pair of electrons on the nitrogen in the amine. The unstable product of this step is stabilized by the loss of an equivalent of water from the molecule to form a Schiff base as shown below [9].

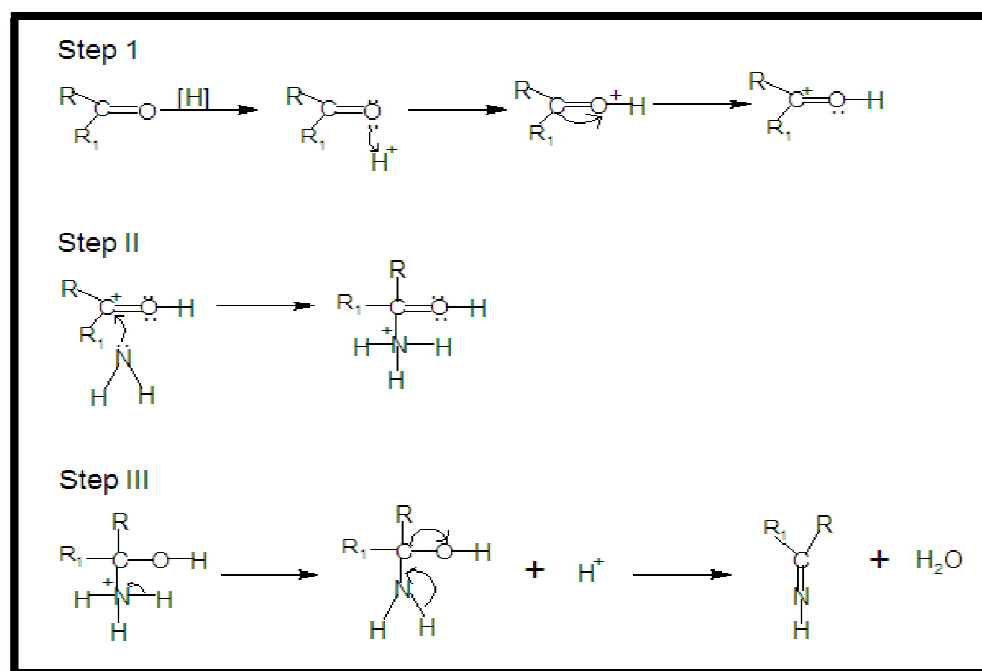


Figure 1

This work is a continuation of similar work done and reported before, therefore it describes the synthesis, characterisation and antimicrobial activities of *p*-nitroanilinesalicylidene and the corresponding Ni(II), Cu(II) and Zn(II) complexes

2. Experimental

All reagents and solvents used in this work were of analytical grade obtained from Sigma-Aldrich and were used as supplied. The elemental analysis was carried out using Perkin Elmer analyzer, IR spectra were recorded on a Perkin Elmer FT-IR spectrophotometer, the electronic spectra were determined in DMSO using double beam PC scanning spectrophotometer (UVD2960), ¹H-NMR spectra were recorded on a Bruker spectropin Avance 400 spectrometer using TMS as an internal standard and DMSO-d₆ as solvent. The magnetic susceptibility was determined by Gouy balance using copper sulphate as standard material. Molar conductance was measured on Jenway 4510 conductivity bridge with conventional dip- type black electrode. All melting points were taken on Gallen Kemp melting point apparatus

2.1. Synthesis of the Ligand

10mmol (0.28g) of *p*-nitroaniline dissolved in 20ml ethanol was slowly mixed while stirring with salicylaldehyde (10mmol,0.24g) in 20ml ethanol. Three drops of glacial acetic acid was added to the mixture and stirred magnetically for two hours. The resulting yellow precipitate was filtered and washed with ethanol then dried over fused calcium chloride

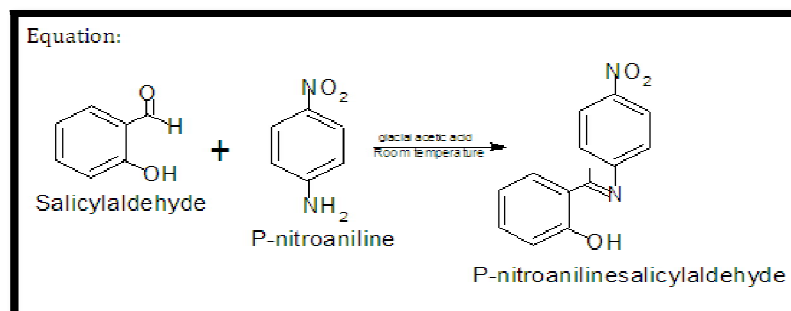


Figure 2

2.2. Synthesis of Complexes

The Schiff base ligand, *p*-nitroanilinesalicylalidene (0.26g,10mmol) was dissolved in 20ml ethanol. To this solution, 20ml of ethanolic solution of 10mmol copper(II) sulphate pentahydrate was added, followed by three drops of glacial acetic acid. The mixture was magnetically stirred for two hours and the precipitate formed was filtered, washed with ethanol and

dried over fused calcium chloride. The weight was taken and percentage yield calculated. The procedure was repeated for all the listed metal (11) salts

2.3. Antimicrobial Activity Test

Standard methods adopted are well documented in many literature [10-12] All the synthesized compounds were screened for antimicrobial activity against a Gram-positive bacterium, *S. aureus*, a Gram-negative, *E. coli*, two fungi - *C. albican* and *A. flavus*. The agar-Paper disc method and the broth diffusion methods were used for bacteria and fungi respectively.

3. Results

| Compound | % Yield | Melting Point (°C) | Molar conductance μs | Colour | Found (Calcd),% | | |
|---|---------|--------------------|---------------------------------|--------------------|------------------|----------------|------------------|
| | | | | | C | H | N |
| PNS $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_4$ | 58.7 | 156.6 | 0.05 | Yellow | 60.10 (59.9) | 4.51 (4.6) | 10.73 (10.76) |
| $\text{Zn}[\text{PNS}]_2$ $\text{ZnC}_{26}\text{H}_{24}\text{N}_4\text{O}_8$ | 68.2 | 172.3 | 0.04 | Grey | 53.5 (52.8) | 4.12 (4.20) | 9.26 (9.50) |
| $\text{Cu}[\text{PNS}]_2$ $\text{CuC}_{26}\text{H}_{24}\text{N}_4\text{O}_8$ | 65 | 155.5 | 0.01 | Greenish yellow | 53.17 (53.47) | 4.10 (4.11) | 9.62 (9.60) |
| $\text{Ni}[\text{PNS}]_2$ $\text{NiC}_{26}\text{H}_{24}\text{N}_4\text{O}_8$ | 52.6 | 146.5 | 0.05 | Green | 53.52 (53.9) | 4.20 (4.15) | 9.70 (9.68) |

Table 1: Physical Characteristics and Elemental Analysis

| Sample | (NH) | (C=C) | (C=N) | (C-O) | (C=N) | λ_{max} | Transition |
|---------------------------|------|-------|-------|-------|-------|--------------------------|--|
| PNS | 3100 | 1560 | 1680 | 1404 | 1320 | 40,543 36480 33080 | $n \rightarrow \delta^*$ $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ |
| $\text{Ni}(\text{PNS})_2$ | 3310 | 1554 | 1604 | 1426 | 1276 | 17850 25995 | $1A_{1g} \rightarrow 1T_{2g}$ INCT |
| $\text{Cu}(\text{PNS})_2$ | 3120 | 1565 | 1589 | 1398 | 1280 | 20820 23531 | ${}^2B_{1g} \rightarrow {}^2E_g$ ${}^2B_{1g} \rightarrow {}^2A_{1g}$ |
| $\text{Zn}[\text{PNS}]$ | 3210 | 1583 | 1610 | 1398 | 1268 | 26487 36820 33520 | INCT $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ |

Table 2: Summary of Spectroscopic Data

3.1. Discussion

The reaction of the *p*-nitroanilinesalicylalidene ligand with Zn(II) Cu(II) and Ni(II) ions yielded the new complexes that are powdery in nature, stable and non-hygroscopic at room temperature. They dissolved in coordinating solvents like DMSO, DMF and acetone and show a range of colours such as yellow, greenish yellow, green and grey. Their relatively high melting points (147-158°C) are obvious indication of their polymeric nature derived from the strong bonding network. The non-electrolytic nature stem from this polymeric moiety which is shown by the very low values of molar conductance in Table 1.

3.2. IR Spectra

The selected IR bands at 3100-3400, 1404, 1680, and 1224 cm^{-1} of the free ligands are assignable to $\nu(\text{OH})$ / $\nu(\text{C-O})$ phenolic stretching modes, $\nu(\text{C=N})$ azomethine, and $\nu(\text{C-N})$ stretching vibrations. The spectrum of the ligand exhibits a medium band at 3049 cm^{-1} which is assigned to $\nu(\text{NH})$ vibration and another at 1530-1500 cm^{-1} assignable to the nitro group on the aromatic ring. The disappearance of a broad band at 3100-3400 cm^{-1} region in the metal complexes indicates the deprotonation of the phenolic hydrogen and the subsequent coordination of oxygen to metal ion. This is evident in the upward shift by 25-86 cm^{-1} of the $\nu(\text{C-O})$ band observed [13]. The spectra of the complexes exhibit a systematic shift in the positions of the bands in the region of 1680-1354 cm^{-1} due to $\nu(\text{C=C})$ and $\nu(\text{C=N})$ vibrational modes and their mixing patterns are different from those in the ligand spectrum. ...

The strong band observed at 1620-1640 cm^{-1} is a clear indication of the coordination of the azomethine nitrogen to the metal ions on complexation. This is further affirmed by the existence of weak bands at 624-432 cm^{-1} suggesting $\nu(\text{M-N})$ and $\nu(\text{M-O})$ linkages. From these, the Schiff base ligand obviously is a bidentate molecule coordinating to the metal through the phenolic oxygen and azomethine nitrogen in the complexes.

3.3. ¹H-NMR Spectrum

¹Proton-NMR spectra of the synthesized compounds were recorded in DMSO-d₆ solution, the ligand gave two singlet signals at δ10.66ppm and δ10.20ppm region which are downfield from TMS and which disappeared upon adding D₂O. The multiplets at δ7.48ppm are assignable to the phenyl ring protons. The characteristic azomethine CH=N peak is at δ8.64-8.86ppm as a singlet. The singlet signal of the phenolic proton (OH) is at δ8.60ppm which disappeared on complexation, affirming the deprotonation and subsequent involvement of the oxygen atom in bond formation.^[2] Electronic Spectra The electronic spectra of the synthesized compounds as displayed in Table 2 were recorded in DMSO solution. The absorption bands for the free ligand, p-nitroanilinesalicylidene at 40543, 36480 and 33,080cm⁻¹ are assignable to the intraligand transitions caused by unsaturation and delocalisation of electrons in the ligand system. The n → δ*, π → π*, n → π* transitions are due to these intraligand transition, lone pair of electron on the heteroatom and double bond of the ligand system. There is a bathochromic shift on complexation resulting in the characteristic bands at 20820, 23531 and 26487 cm⁻¹ in the Cu(II) complex assignable to the transitions ²B_{1g} → ²E_g, ²B_{1g} → ²A_{1g} and intra-ligand charge transfer bands. Combining these data and a magnetic moment of 1.72 MB, square planar geometrical configuration is revealed to be the structure of this complex ^[3,14]. The Ni(II) complex has two bands at 17,850 and 25,995 cm⁻¹ assignable to ¹A_{1g} → ¹T_{2g} transition and charge transfer transition. Similarly, the spectral data in combination with a zero value for magnetic moment as a result of the diamagnetic nature of the metal ion confer a square planar geometry to this complex. The electronic absorption spectra of Zn(II), a 3d¹⁰ and diamagnetic ion, also has bands within the region 36820-33520cm⁻¹ due to the n → π* and π → π* intraligand transitions and charge transfer. In the spectra of the complexes, the less intense and broad bands in the 36820-33520cm⁻¹ range result from the overlap of the low-energy π → π* transitions mainly localized within the imine chromophore and the LMCT transition from the lone pair of the phenolate oxygen donor to the metal ion, in this case Zn (II) ion ^[15], thus, giving a tetrahedral geometrical complex Fig.1 below:

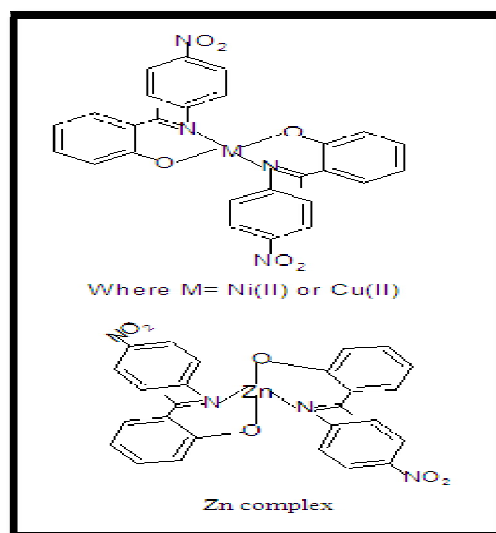


Figure 3

3.4. Antimicrobial Activity

The antimicrobial activities of the synthesized compounds show that the inhibitory action of the ligand on the growth of the mentioned microbes is less than those of the metal complexes. This is in conformity to many other reported cases that the complexes antimicrobial effectiveness is almost always higher than that of the ligand. ^[1,2,3].

4. Conclusion

Novel Ni(II), Cu(II) and Zn(II) complexes have been synthesized and characterized, the bidentate ligand, p-nitroanilinesalicylidene coordinate to the metal ions through the phenolic oxygen and azomethine nitrogen giving square planar geometrical configurations to Ni(II) and Cu(II) complexes while the Zn(II) complex adopt the tetrahedral geometry. These complexes possess higher degrees of inhibitory actions on Staphylococcus aureus, Echerichia coli, Candida albican and Aspergillus niger than the free Schiff base ligand from which they are made from.

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